Micromechanical Modeling of the Binder Material of PBX 9501

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Theoretical Division participates in the important but extremely difficult materials science task of predicting the lifetime of nuclear weapons. As part of Los Alamos National Laboratory's (LANL's) Enhanced Surveillance Campaign, we study PBX 9501—a plastic-bonded high explosive (HE) composed of a 1:1 (by weight) mixture of a nitroplasticizer (NP) and a polyurethane (Estane® 5703). Estane® is copolymer composed of multiple methyl di-isocyanate (MDI) units connected by random lengths of polyester. The weight-averaged molecular weight is approximately 80 K Daltons. Over a time period of weeks, some of the hard segments (MDI units) phase separate, forming a three-dimensional (3D) random network of nodes (MDI units) and chains (polyester soft segments). The binder derives its mechanical strength by virtue of this highly interconnected network.

Chemical and physical changes that occur as the binder material ages will affect its mechanical properties, and this can impose an ultimate lifetime on the HE charge. How the NP affects the mechanical properties of the binder has been an important issue. A straightforward analysis of tensile stress/strain experiments that covered a range of Estane®:NP mixtures suggests that the NP acts mostly as a diluent in the binder. Figure 1 shows the tensile stress at various strains as a function of the NP fraction ($f_{NP} = 1 - f$), where f is the weight fraction of Estane®.

We fit the experimental data to various power laws and find that the relation $S = S_o f^3$ provides reasonable agreement for strains between 100% and 900%. Although the experiments did not explicitly include the case of 100% NP ($f = 0$), it is obvious that since NP is a liquid, the stress must go to zero (if the Estane® fraction is zero, then no network can exist). Clearly, one factor of f suffices to impose this condition. Our conjecture is that the other factor of f^2 represents a network formation probability, i.e., the probability that two MDI units will bind together to form a hard domain is proportional to the square of the local MDI density. This would be analogous to a reaction rate for classical gas phase dimerization being proportional to the square of the monomer concentration. In this case, however, it is
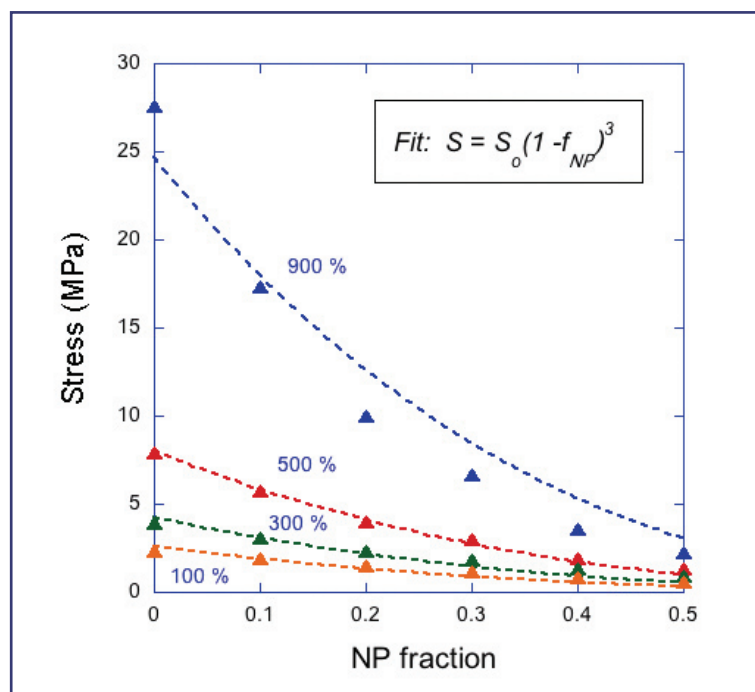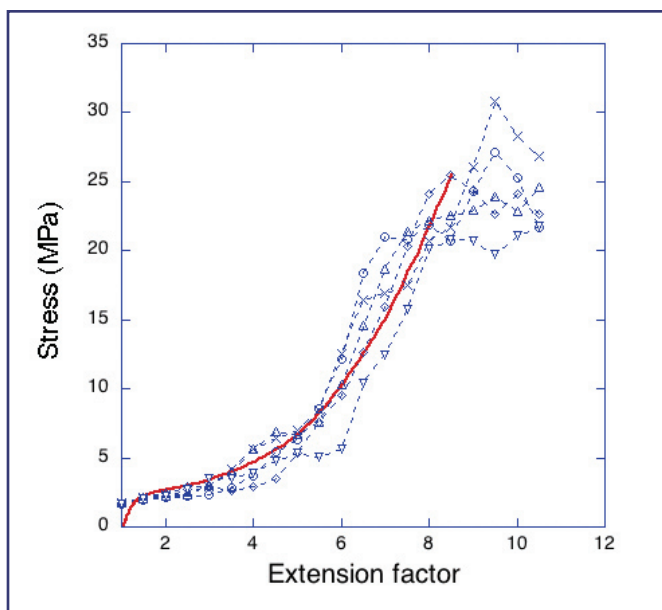

Figure 1—
Least square fits of the experimental tensile stress (Bruce Orler, from Group MST-7 at LANL) to the cube of the Estane® weight fraction ($S = S_o f^3$), parametric on strain.

Fit: $S = S_o (1 - f_{NP})^3$

the time-integrated rate that matters, so the analogy is not perfect. Establishing that the NP acts as a diluent provides confidence that theoretical and experimental studies of neat Estane® are relevant to understanding the behavior of the binder. Although the influence of NP on mechanical properties appears to be simple, that is not the case for the chemical degradation of the Estane®; here the role of NP appears to be quite complex [1].

Previously, under Laboratory-Directed Research and Development funding, we developed an explicit, 3D numerical network model (EPnet) [2] to simulate the micromechanical behavior of cross-linked and/or filled polymers (e.g., silica-filled polydimethylsiloxane) for various static strains. The molecular forces required to stretch a chain or disrupt its binding to a filler particle were estimated from atomistic simulations. Because the network produced by the polymer phase separation in Estane® yields a node-and-chain morphology similar to that of a filled polymer, we believe that we can apply this model to the study of Estane®. Figure 2 shows a comparison of five statistically independent random network simulations (dashed lines) compared to a tensile stress/strain experiment by Bruce Orler, from the Polymers and Coatings Group (MST-7) at LANL (solid line).

The volume element simulated (a 90-nm cube) included 1500 nodes interconnected by about 8000 chains. Parameter values used in the model, which were adjusted to obtain agreement with experiment, are consistent with estimates obtained from atomistic simulations or experimental data. Not only does the model provide a quantitative prediction for the yield stress, but it is also able to capture the phenomenon of tensile failure. The agreement between simulation and experiment is an important result because it gives us confidence that we understand the mechanisms that produce strength in the HE binder. We will use this picture to understand how chemical changes can affect the mechanical properties.

[1] Denise K. Pauler and Joel D. Kress, "Decomposition of Nitroplasticizer in Plastic-Bonded Explosive PBX 9501," in this volume on p. 58.
[2] D.E. Hanson, *Polymer* **45**, 1055 (2004).

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